8-20-2017

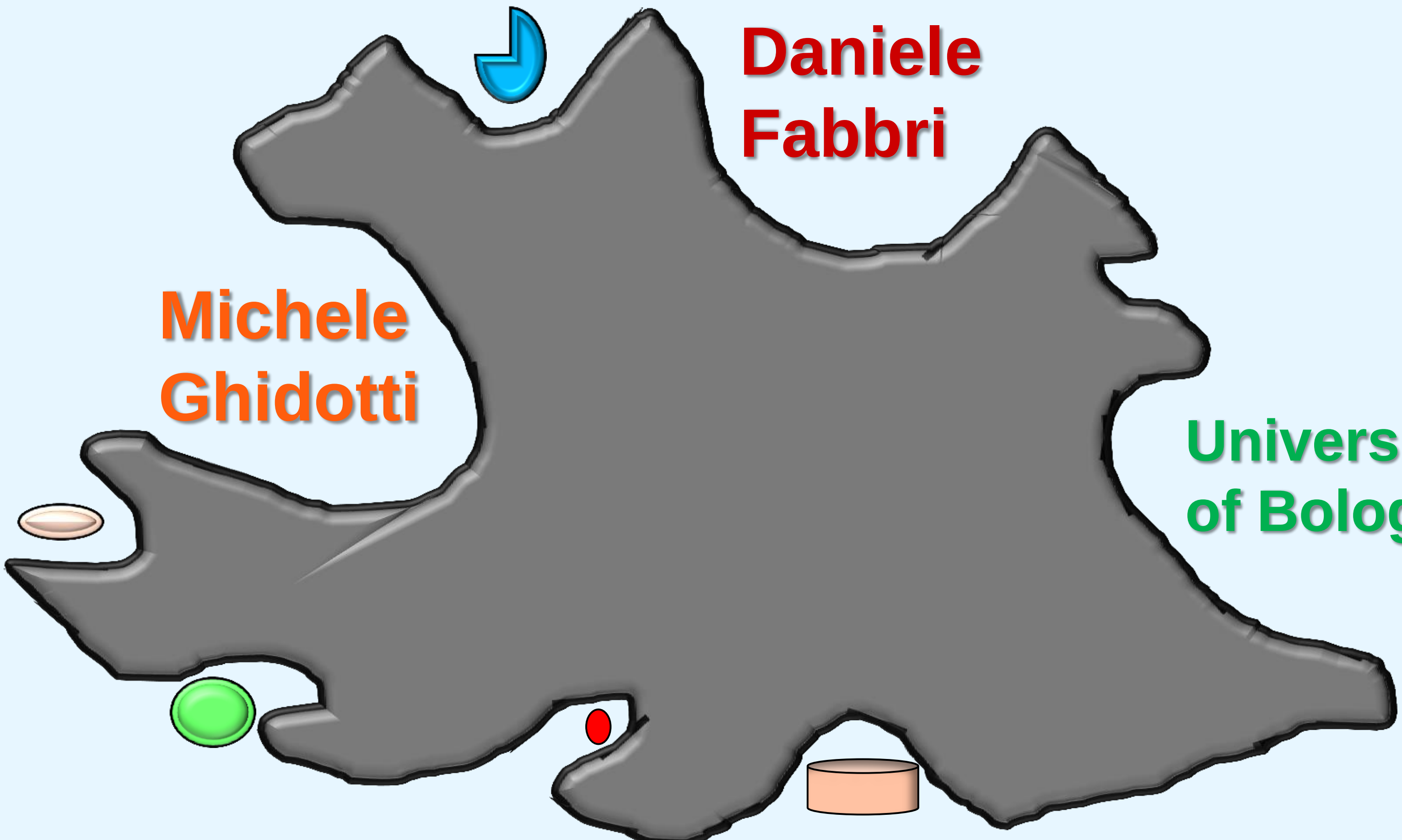
Mobile organic compounds in biochar. Relationships with carbonization degree and bio-oil composition

Daniele Fabbri
University of Bologna, Italy

Michele Ghidotti
University of Bologna, Italy

MOBILE ORGANIC COMPOUNDS in BIOCHAR

Relationships with carbonisation degree and bio-oil composition



Daniele Fabbri

Michele Ghidotti

University of Bologna

Mobile compounds importance

Source: PSR 2014-2020 RER RIFASA

migration to water

emission to air

soil-biota interaction

dissolved organic carbon dynamic

Origin, characterisation, effects

Qualitative analysis of volatile organic compounds on biochar

Kurt A. Spokas [a,b,*], Jeffrey M. Novak [c], Catherine E. Stewart [d], Keri B. Cantrell [a], Minori Uchimiya [e], Martin G. DuSaire [a], Kyoung S. Ro [c]

[a] United States Department of Agriculture, Agricultural Research Service, Soil and Water Management Unit, Saint Paul, MN, USA
[b] Department of Soil, Water, and Climate, University of Minnesota, Saint Paul, MN, USA
[c] United States Department of Agriculture, Agricultural Research Service, Coastal Plains Soil, Water, and Plant Research Center, Florence, SC, USA
[d] United States Department of Agriculture, Agricultural Research Service, Soil Plant Nutrient Research, Fort Collins, CO, USA
[e] United States Department of Agriculture, Agricultural Research Service, Southern Regional Research Center, New Orleans, LA, USA

Chemosphere 85 (2011) 869–882

Characterization of biochar-derived dissolved organic matter using UV–visible absorption and excitation–emission fluorescence spectroscopies

Tyler Jamieson [a,b], Eric Sager [c], Céline Guéguen [b,*]

[a] Environmental and Resource Studies Program, Trent University, Peterborough, ON, Canada
[b] Department of Chemistry, Trent University, Peterborough, ON, Canada
[c] Sir Sanford Fleming College, Lindsay, ON, Canada

Chemosphere 103 (2014) 197–204

Pyrolysis temperature-dependent release of dissolved organic carbon from plant, manure, and biorefinery wastes

Minori Uchimiya [a,*], Tsutomu Ohno [b], Zhongqi He [a]

[a] USDA-ARS Southern Regional Research Center, 1100 Robert E. Lee Boulevard, New Orleans, LA 70124, USA
[b] Department of Plant, Soil, and Environmental Sciences, University of Maine, 5722 Deering Hall, Orono, ME 04469, USA

Journal of Analytical and Applied Pyrolysis 104 (2013) 84–94

Organic compounds leached from fast pyrolysis mallee leaf and bark biochars

Caroline Lievens [*], Daniel Mourant, Richard Gunawan, Xun Hu, Yi Wang

Fuels and Energy Technology Institute, Curtin University of Technology, GPO Box U1987, Perth, WA 6845, Australia

Chemosphere 139 (2015) 659–664

Profiles of Volatile Organic Compounds in Biochar: Insights into Process Conditions and Quality Assessment

Michele Ghidotti,[*,†] Daniele Fabbri,[†] and Andreas Hornung[‡]

[†] Interdepartmental Centre for Industrial Research "Energy and Environment" and CIRSA, University of Bologna, via S. Alberto 163, I-48123 Ravenna, Italy
[‡] Fraunhofer Institute for Environmental, Safety, and Energy Technology UMSICHT, Institute Branch Sulzbach-Rosenberg, An der Maxhütte 1, 92237 Sulzbach-Rosenberg, Germany

ACS Sustainable Chem. Eng. 2017, 5, 510–517

Mobile organic compounds in biochar — A potential source of contamination — Phytotoxic effects on cress seed (*Lepidium sativum*) germination

Wolfram Buss, Ondřej Mašek [*]

UK Biochar Research Centre, School of GeoSciences, University of Edinburgh, Crew Building, King's Buildings, Edinburgh EH9 3JN, UK

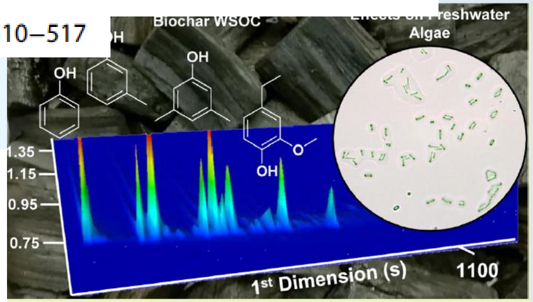
Journal of Environmental Management 137 (2014) 111–119

Investigation into the Sources of Biochar Water-Soluble Organic Compounds and Their Potential Toxicity on Aquatic Microorganisms

Cameron R. Smith,[†] Patrick G. Hatcher,[†] Sandeep Kumar,[‡] and James W. Lee[*,†]

[†] Department of Chemistry and Biochemistry, and [‡] Department of Civil and Environmental Engineering, Old Dominion University, 4541 Hampton Boulevard, Norfolk, Virginia 23529, United States

ACS Sustainable Chem. Eng. 2016, 4, 2550–2558



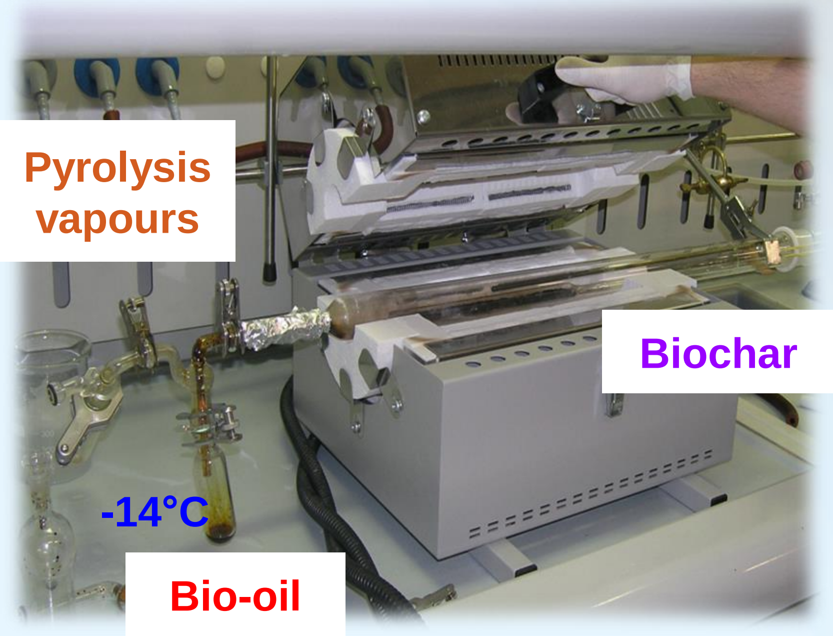
Aims

Analysis
Water soluble organic compounds

Relationships between the composition in biochar and the corresponding bio-oil

Produced from the same biomass (corn stalk) at different pyrolysis temperatures

Biochar and bio-oil samples



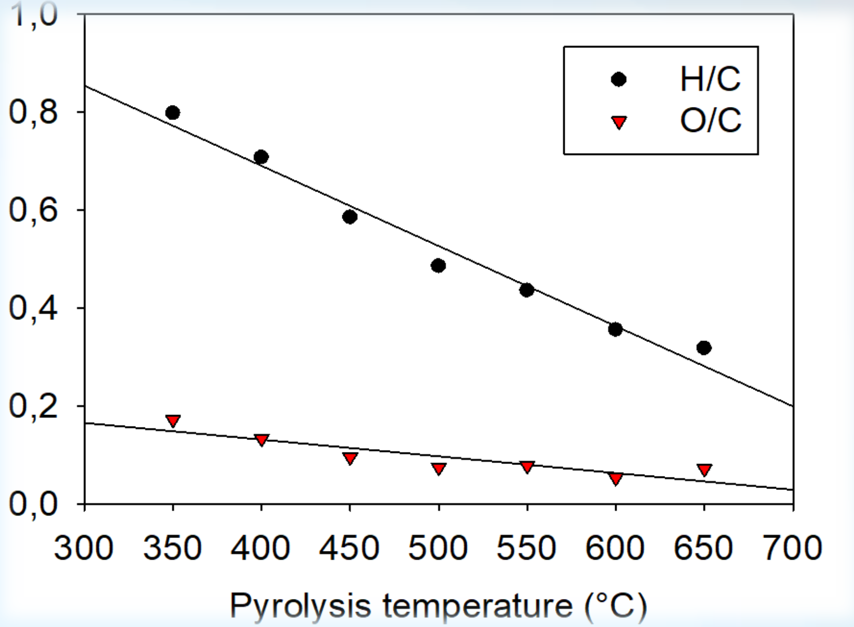
N_2 *flow 1 L /min*

Heating rate ~ 0.8 °C/s
Holding time = 20 min

Pyrolysis °C ***350*** → ***650***

Vapours °C ***195*** → ***310***

Water soluble organic compounds



Seven biochar samples with different H/C ratios From 0.8 to 0.3

350 **450** **550** **650 °C**

Biochar water extracts 1g:10 mL 72 h r.t.

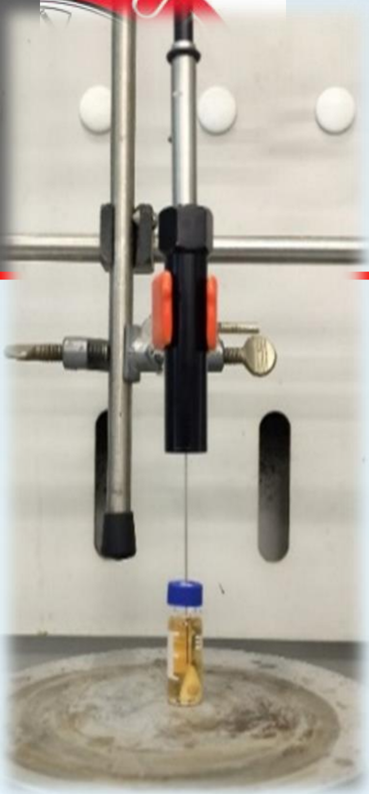
Bio-oil water extracts 1:10 v/v

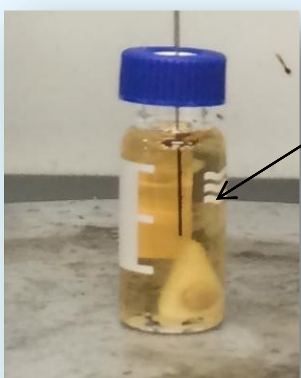
Method-based compound classification

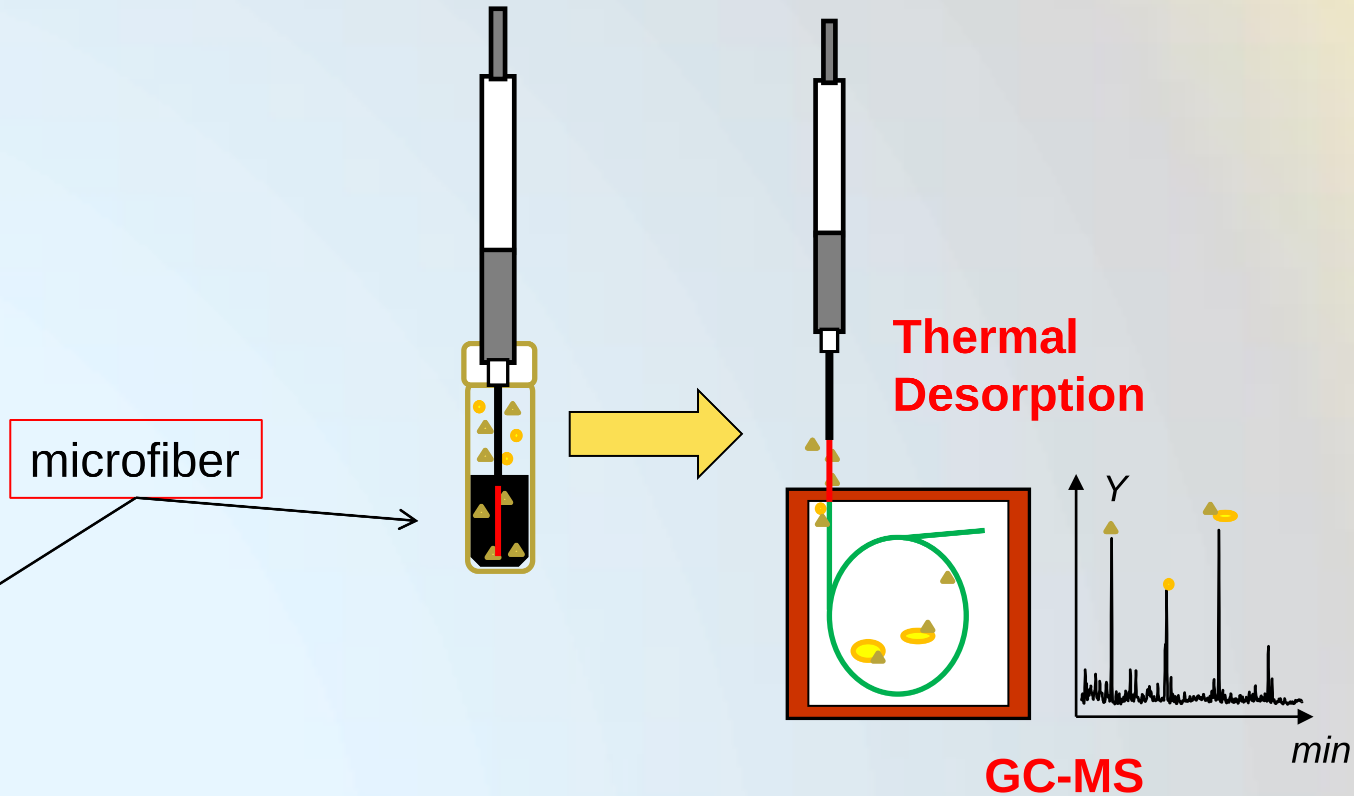
Chemical typology	*Analytical method*	*Information*
SEMIVOLATILE more volatile	SPME // GC-MS	Structural formula
HYDROPHILIC less volatile	ESI (-) – FTICR-MS	Molecular formula
UNSATURATED Conjugated – any volatility	FLUORESCENCE SP.	“Bulk”

Semivolatile

Chromatography with SPME solid-phase microextraction







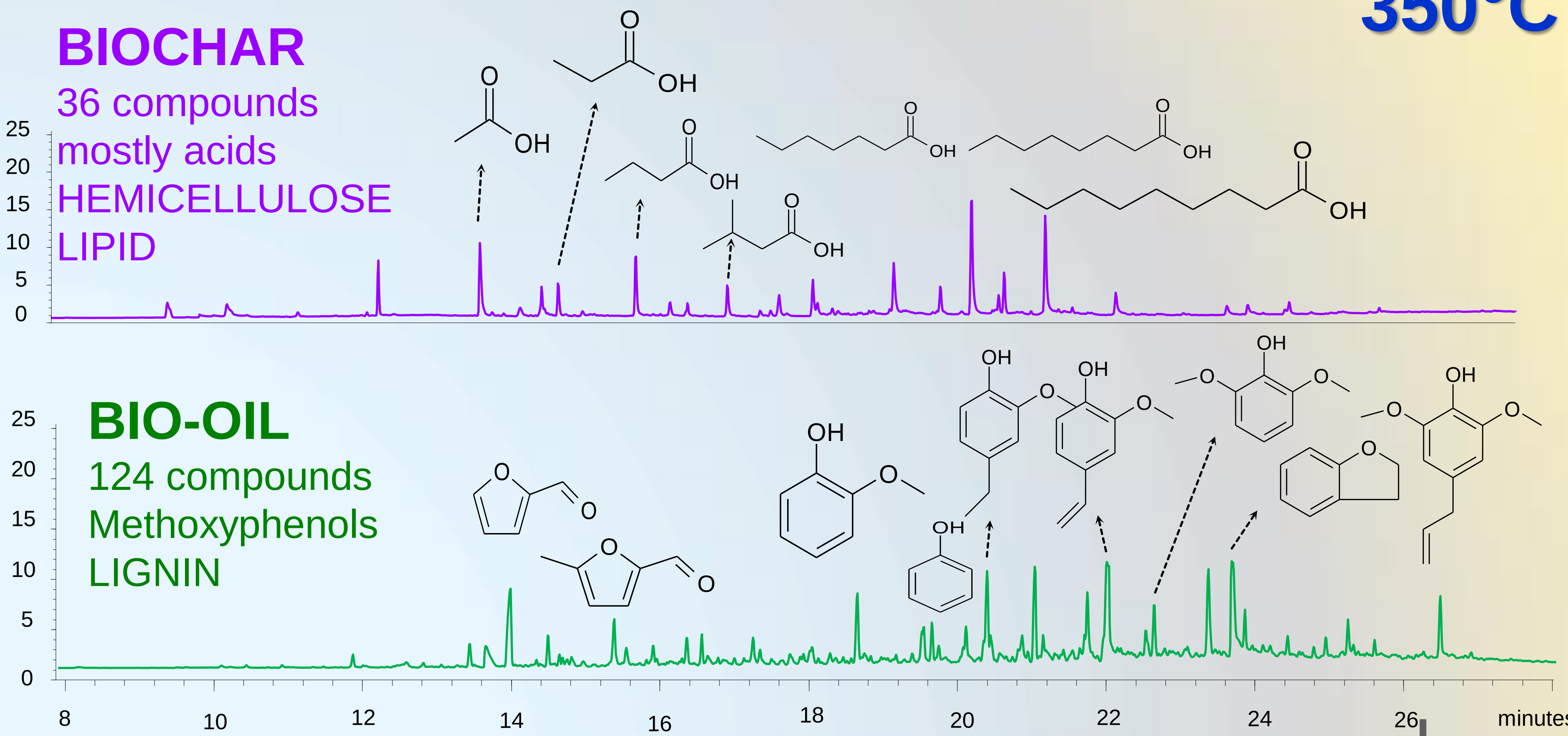
1 ml water extract + 0.5 mL 2 M phosphate buffer at pH 5.7 , 30 min with Car-PDMS fiber

Bio-oil vs biochar

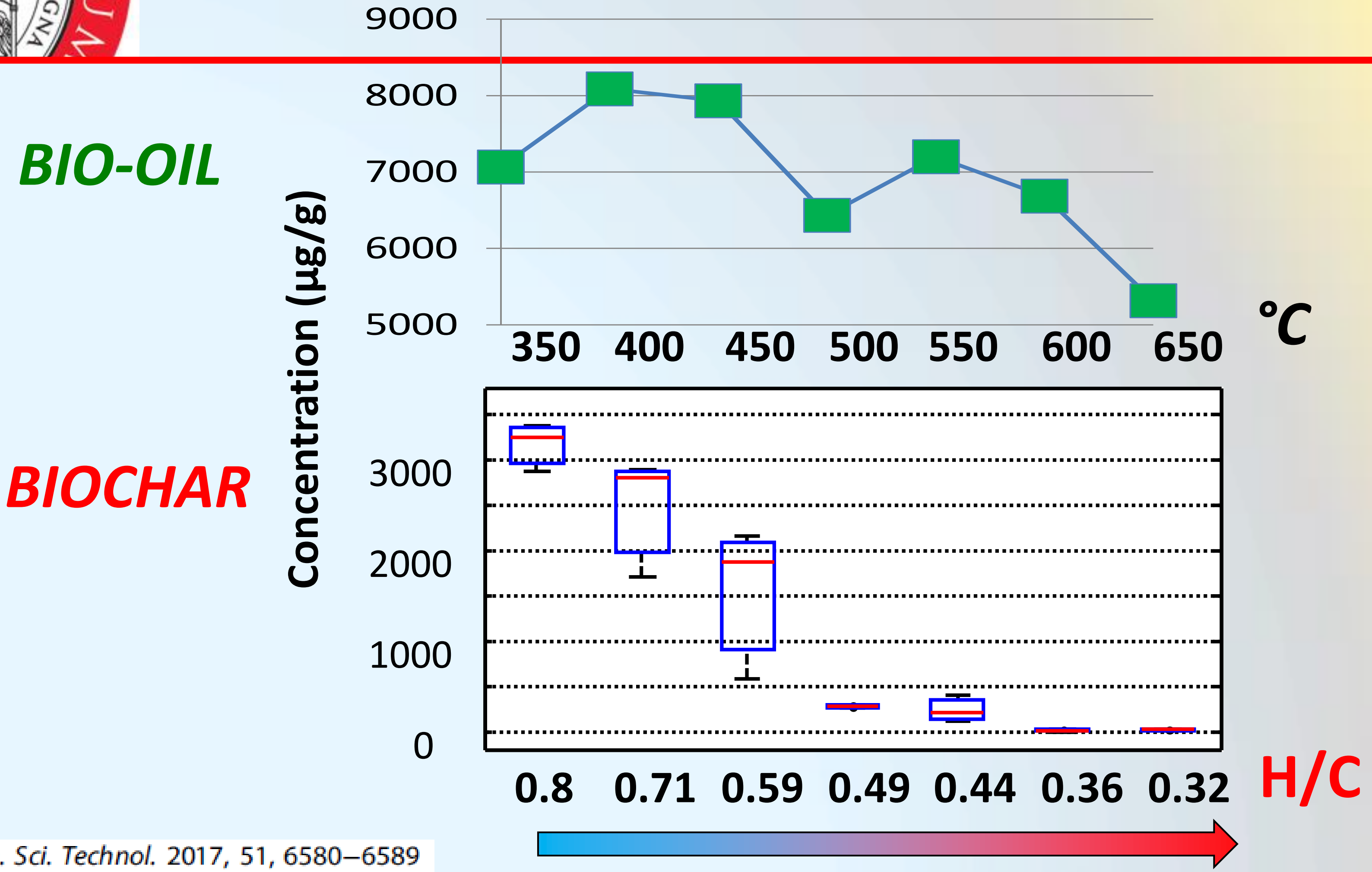
350°C

BIOCHAR
36 compounds
mostly acids
HEMICELLULOSE
LIPID

BIO-OIL
124 compounds
Methoxyphenols
LIGNIN



Volatile fatty acids



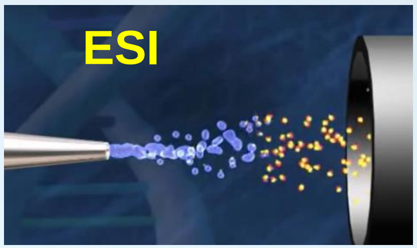
Environ. Sci. Technol. 2017, 51, 6580–6589

Hydrophilic

high resolution mass spectrometry

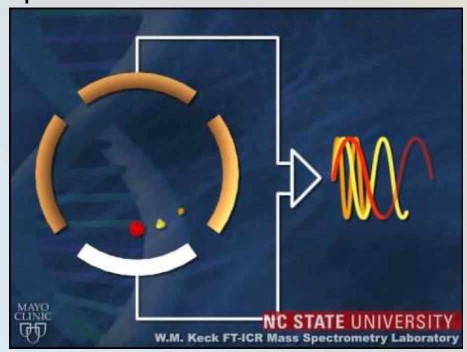
Source
http://jlab.chem.yale.edu/research/techniques/

IONISATION

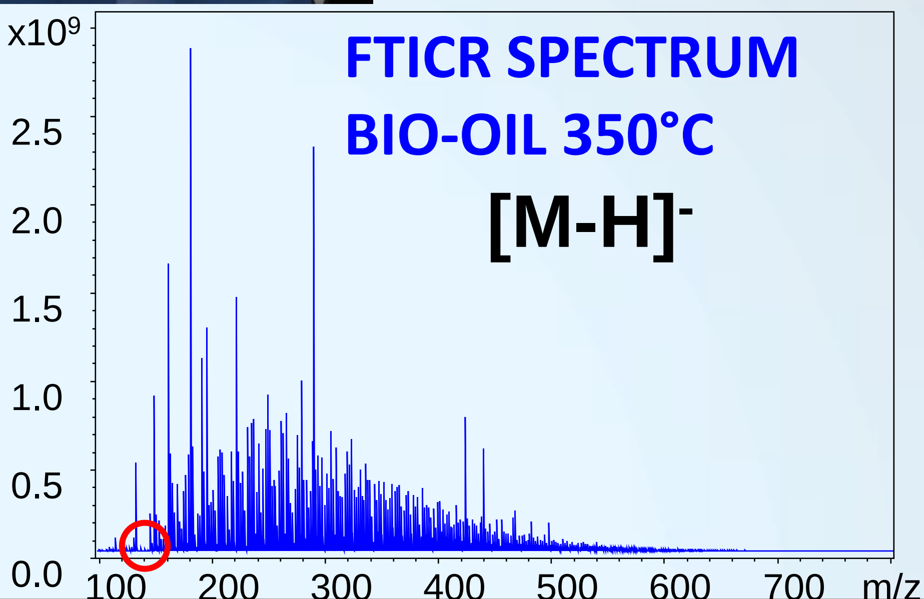


ESI (-)
Negative ion electrospray ionisation

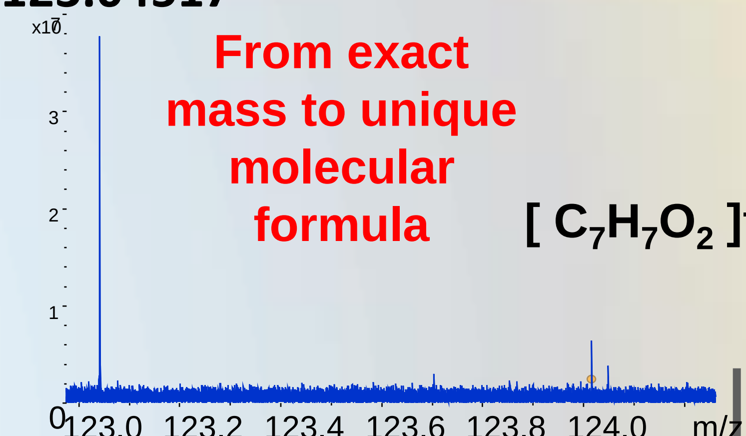
ION SEPARATION



FT-ICR
Fourier transform ion cyclotron resonance



123.04517



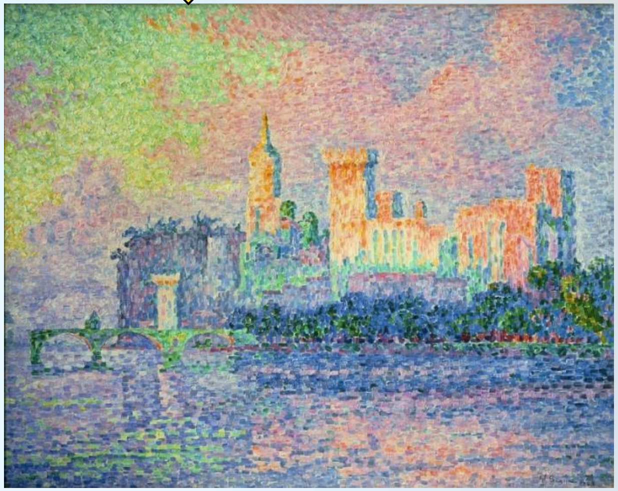
From exact mass to unique molecular formula

$[C_7H_7O_2]^-$

Picturing thousands of peaks

Number of peaks (compounds)

°C	BIO-OIL	BIOCHAR
350	3267	2207
650	3925	40

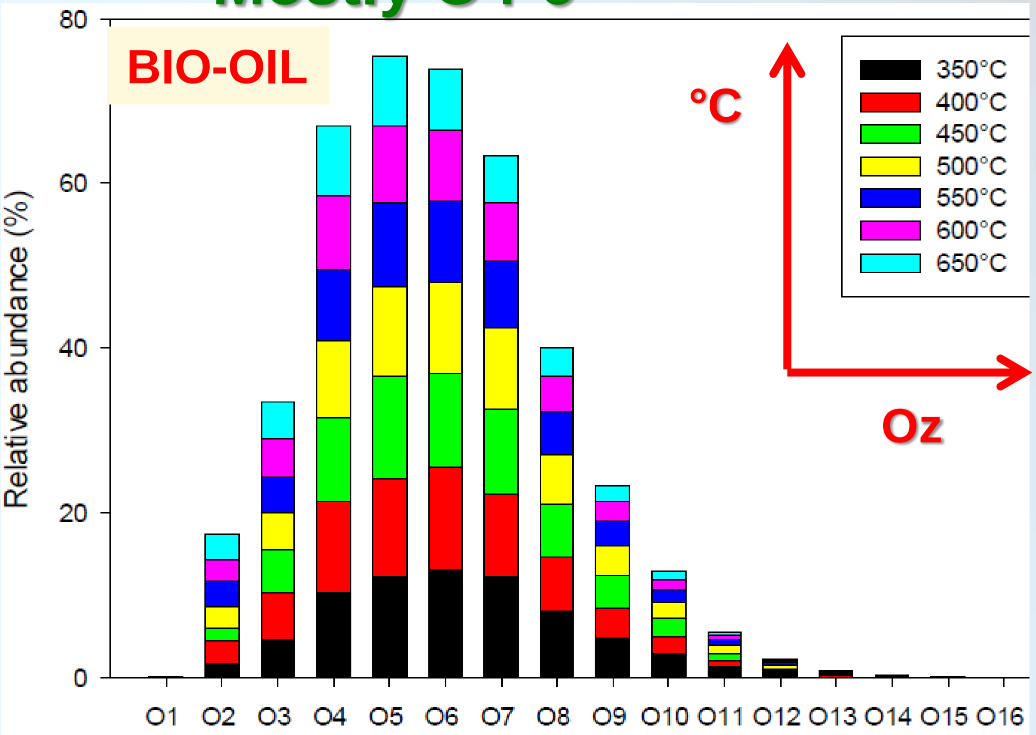


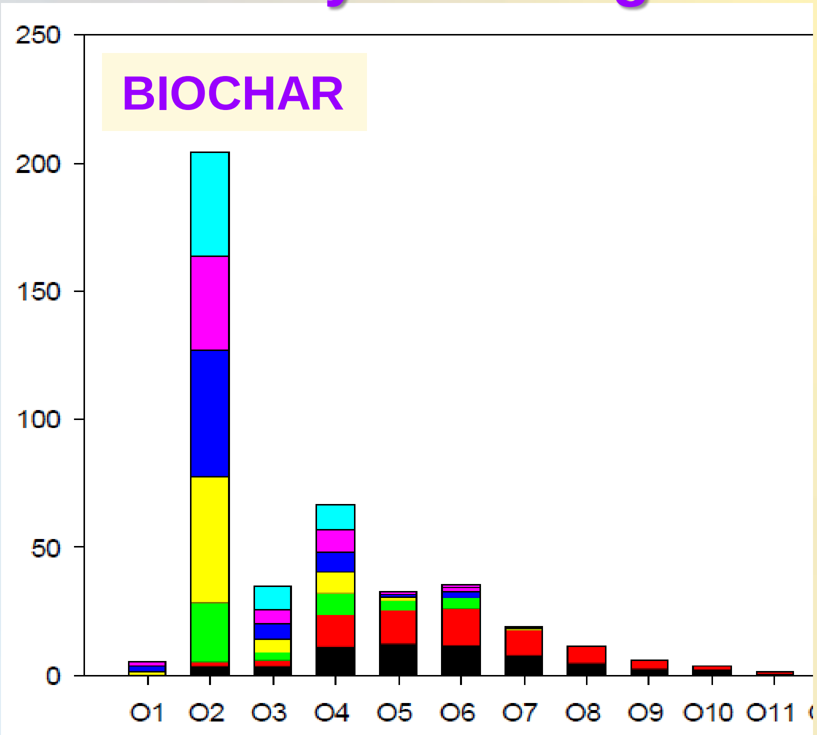
Pual Signac, Palais des Papes Avignon,Musee d’Orsay, Paris. Source::wikimedia commons

Distribution of CxHyOz

BIO-OIL
Mild T effect
Mostly O4-6

BIOCHAR
Strong T effect
Mostly O2 at high T





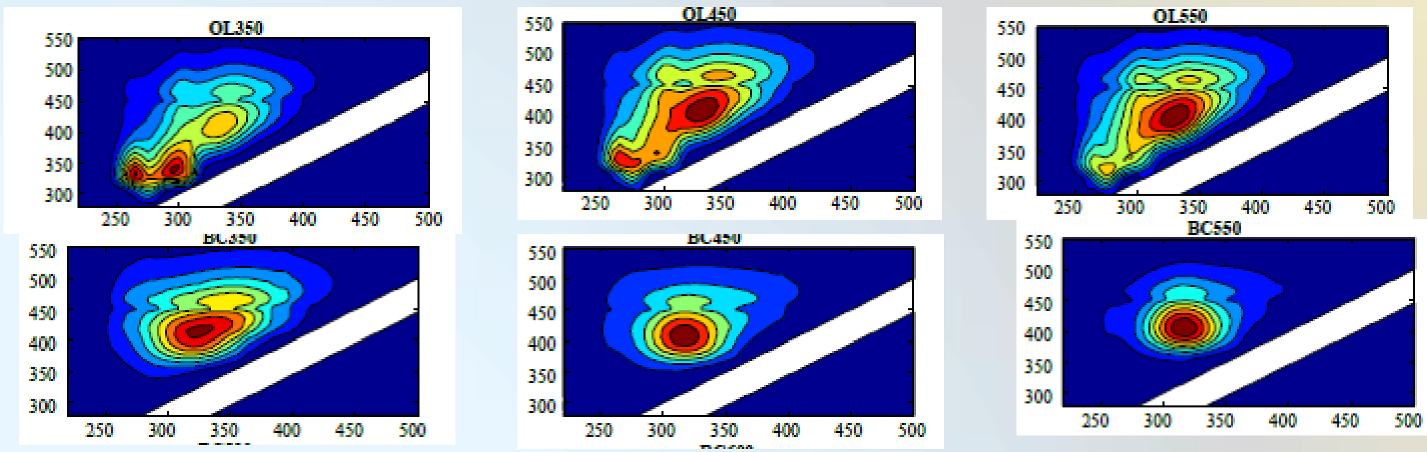
Environ. Sci. Technol. 2017, 51, 6580–6589

Analytical Pyrolysis

Fluorescence spectroscopy

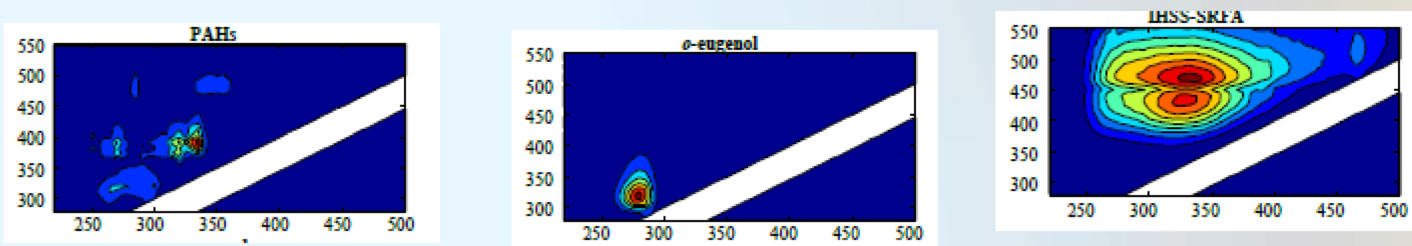
excitation/emission matrices

350 °C | 450 °C | 550 °C



BIO-OIL

BIOCHAR



Model compounds

PAHs

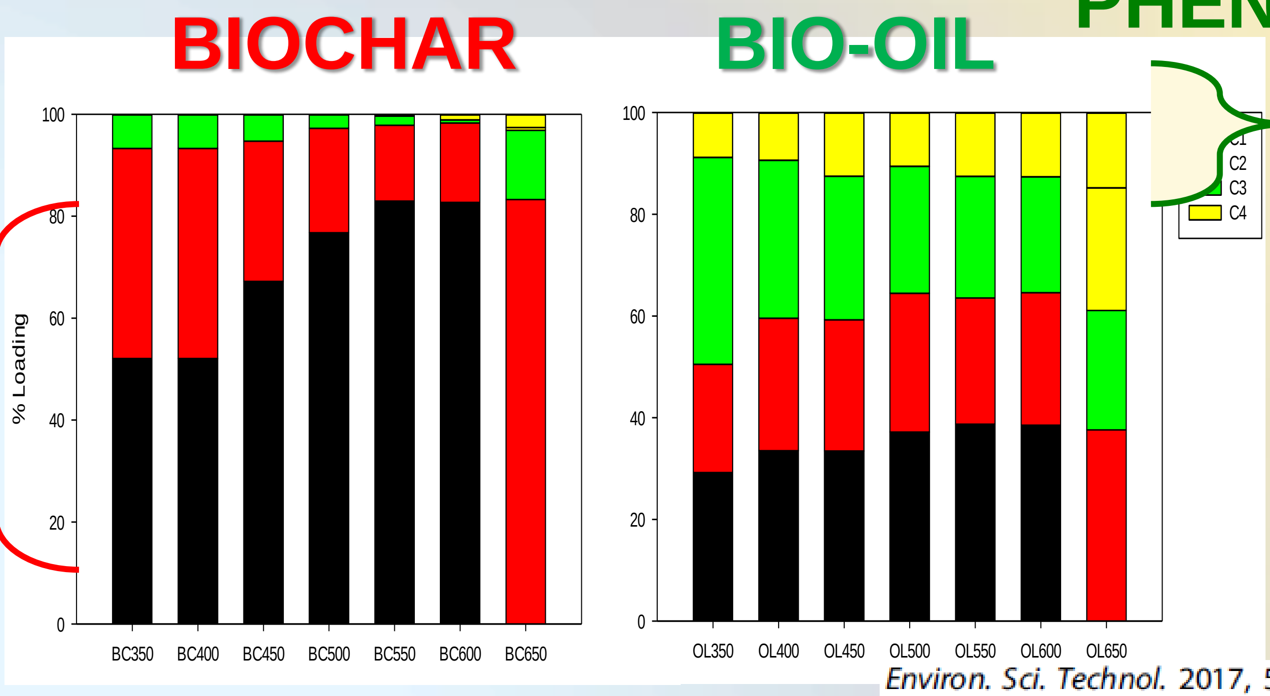
Lignin phenols
o-eugenol

Fulvic acids

PARAFAC

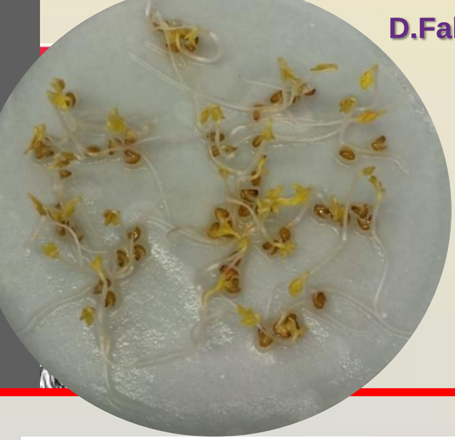
LIGNIN-PHENOLICs

FULVIC-LIKE



Environ. Sci. Technol. 2017, 51, 6580−6589

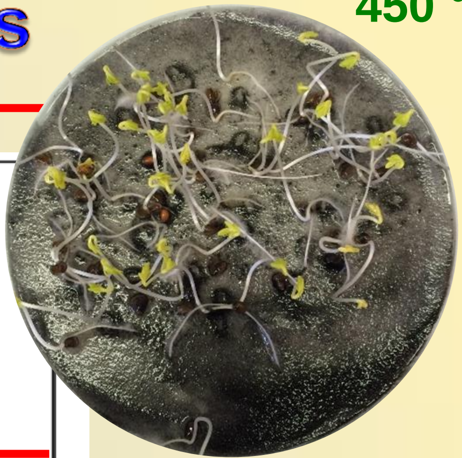
Fluorescence signals decomposed into underlying **four** individual fluorescence components: C1-2 phenols, C3-4 humics

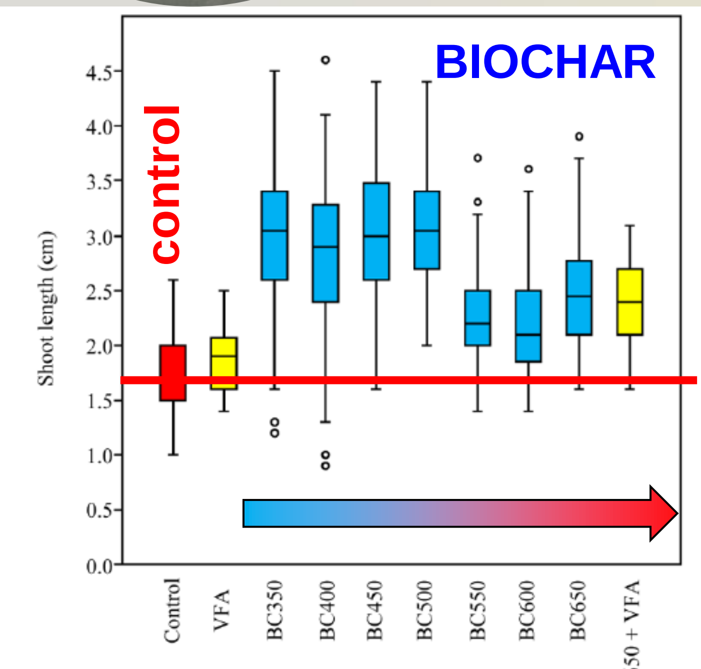


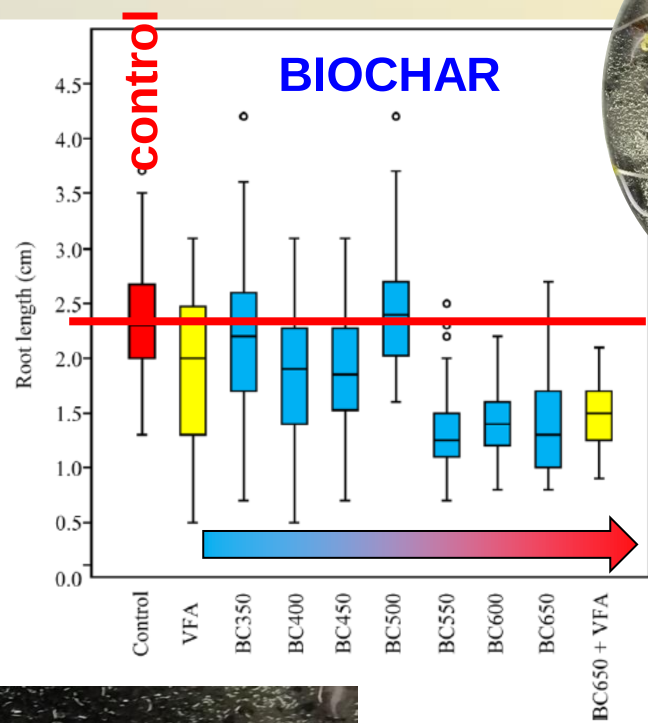
control

Implications
cress germination tests

450 °C







Fulvic acid-like structures could be associated to improved shoot growth

SHOOT length

promoted

ROOT length

reduced

Environ. Sci. Technol. 2017, 51, 6580−6589

Combining analytical results

The pattern of WSOCs in bio-oil was not affected by pyrolysis temperature: it is essentially build up at 350-400 °C

The pattern of WSOCs in biochar was significantly different from that of bio-oil and the abundance decreased with increasing pyrolysis temperature.

Increasing carbonisation reduces the extent of pyrolysis products sorbed by biochar and their migration into water.

favours the release of components similar to soil organic matter.